THE TRUE ATOMIC WEIGHT OF BROMINE.

(Plates XXXIV.–XXXVI.)

By DR. GUSTAVUS HINRICHS.

(*Read April 4, 1913.*)

Highly important laboratory work, undertaken for the purpose of determining the atomic weight of bromine, has quite recently been done by Dr. H. C. P. Weber.[1] Ten complete syntheses of hydrogen bromide were made, taking from 60 to 80 grammes of bromine for the individual determinations.

Employing the method of reduction in general use by the dominant school, Mr. Weber finds the atomic weight of bromine to be 79.924 with the insignificant "*probable error*" of 0.0014, oxygen at 16 exactly being taken as the standard.[2] Accordingly, the atomic weight of bromine should fall between 79.923 and 79.925, for $O=16$.

Now bromine is one of the ten fundamental elements of the system of Stas (Ag, Pb, Na, Ka; Cl, Br, Io; N, S, O). If the above value for Br should be found to be in error, such error would affect the values of most of the other nine elements also.

During the last twenty years, I believe to have demonstrated,[3] by close mathematical examination of all the atomic weight determinations made during the entire century (since Berzelius began this work in 1810) that the method in common use for the *reduction* of

---

[1] *Jrnl. Am. Chem. Soc.,* Oct., 1912, pp. 1294–1310.

[2] *L. c.,* pp. 1309–1310.

[3] *Special Works:* "True Atomic Weights," 1894; "Absolute Atomic Weights," 1901; "Proximate Constituents," 1904. *Twenty-five Notes* in the *Comptes Rendus,* in twelve years from 1892 to 1912; (in nine years no note on atomic weights); *Moniteur Scientifique,* thirteen papers from 1906–1909; *Revue générale de Chimie,* 1910, on hydrogen; *Proceedings American Philosophical Society,* 1910, 1911; *Proceedings Am. Assoc. Adv. Science,* 1869.

the laboratory work done is not correct but false in principle and erroneous in its results.

Very naturally the dominant school has first denounced my work and thereafter ignored the same; nevertheless it has been compelled to admit the existence of grave errors in the results of Stas which had been extolled to be of astronomical precision. This applies especially to the most famous of the fundamental determinations of Stas, namely those of Ag and N. For nitrogen, Stas gave the value 14.044 exactly. By a marvelous series of decimals (from 38 to 375 places furnished him by A. Quetelet) he declared the lowest *possible* value to be 14.040; at present, the school of Stas has come down to 14.008 which is one fifth of the lowest possible value of Stas and only 8 thousandths above the value we believe to have proved to be the true value, namely 14 *exactly*.[4] For silver the value of Stas has been reduced by his school from 107.930 to 107.880, which is a reduction of fifty thousandths. It must be borne in mind that this matter is a question of high precision, questioning the thousandths of the unit of atomic weights.

All the above values refer to the oxygen standard in common use, O = 16 exactly, for which we believe to have proved that Ag is 108 *exactly* and Br 80 *exactly*. Hence the present values of the dominant school would be 0.120 low for Ag, *i. e.*, 0.11 per cent. of 108; and 0.076 low for Br, *i. e.*, 0.10 per cent. of 80.

If our results are correct, the dominant school is *one tenth of one per cent. low* on the atomic weight of these two fundamental elements.

Accordingly, if our work be true, all the quantitative chemical analyses made in the chemical laboratories throughout the world, from the lowest technical to the highest scientific institutions, have for half a century been falsified (unintentionally, of course, but de facto) to the extent of *one tenth of one per cent.* for both silver and bromine determinations. For lithium, the error committed is now fully one per cent.

---

[4] The experiments of Guye and his students at Geneva are claimed to prove N = 14.008; but each set of determinations has been made within very narrow limits and with small weights at that, except those of 1912, which positively prove N = 14.000, as I have shown (*Comptes Rendus,* May 6, 1812; T. 154, p. 1227).

The question here raised is therefore of the highest practical as well as scientific importance; most assuredly, it cannot be settled by a ballot, though such has recently been taken. Nor should it be left to the decision of a select few for each country, but every individual chemist should, on this as on any other important chemical question, try to study sufficiently to enable him to form an opinion of his own.

To facilitate such a study on the part of the individual chemist, we here present the laboratory work of Mr. Weber on bromine in the most simple and direct way possible, without any refined technicalities: *simply plotting the experimental results themselves* (the ratios of the actual weights) *according to the weight of the bromine taken and the ratios found in each case.*

When the individual chemist inspects this diagram of the actual weights taken and the ratios found, he will realize that we have neither hypotheses to make nor theories to defend. We simply have tried to look at the actual experimental data obtained in the laboratory itself. We have divided the entire process into twelve consecutive steps, each one being distinct and preparatory to the next.

I. THE WEIGHTS, TAKEN AND FOUND.

TABLE I.

WEIGHTS, IN GRAMMES, TO ONE-TENTH MGR.

No.	H	Br	HBr	Discrepancy,[5] Mgr.
1	0.7730	61.2884	62.0605	−0.85
2	0.8606	68.2503	69.1114	0.54
3	0.7761	61.5573	62.3220	−1.42
4	0.9693	76.8822	77.8514	−0.15
5	1.0755	85.2956	86.3709	−0.15
6	0.9969	79.0683	80.0642	−0.99
7	0.7497	59.4528	60.2050	2.59
8	0.9816	77.8555	78.8376	0.43
9	1.0013	79.3963	80.3966	−0.06
10	0.8198	65.0214	65.8387	−2.56
Sum	9.0037	714.0572	723.0583	−2.63
Means	0.9004	71.4057	72.3058	−0.26

[5] The discrepancy is: HBr — (H + Br) and its theoretical value is 0, of course. The actual value is once over 1 and twice over 2 mgr.: hence the hundredth mgr. of weighings have properly been dropped by me in copying the weights given by Weber.

II. The Analytical Ratio.

TABLE II.

The Analytical Ratio, *r*; Calculated to 6 Decimals, the Sixth as First to the Fifth, Since Ordinarily Only Fifth is Taken.

	Ratio:	1st	2d	3d
	Br (to 1st dec.)	H/Br	H/HBr	Br/HBr
1	61.3	0.012 61.2	0.012 45.6	0.987 55.8
2	68.3	60.9	45.2	56.3
3	61.4	61.0	45.3	57.1
4	76.9	60.7	45.1	55.1
5	85.3	60.9	45.2	55.0
6	79.1	60.8	45.1	56.2
7	79.5	61.0	45.2	50.6
8	77.9	60.8	45.1	54.3
9	79.4	61.1	45.4	55.8
10	65.0	60.8	45.2	58.6
Mean	71.4	60.9	45.2	55.5
Range	23.8	0.4	0.5	8.0

Remarks.—(1) Ratios very concordant; range small, especially in first and second (five significant digits only), less so in third (six significant digits). (2) The reciprocal ratios of nos. 1 and 2 would magnify the minute error in H eighty-fold. (3) Complete synthesis gives the three equally important ratios; Weber omits no. 3.

III. The Variation of the Analytical Ratio.

As soon as the individual determinations of the analytical ratio *r* (Table II.) are plotted according to a convenient scale it is seen that this ratio is not constant, but variable. In our drawing (No. 750) the abscissæ represent the weight *w* of bromine taken on the scale of a centimeter to the gramme, while the ordinates represent the corresponding ratio *r* on the scale of one inch to the unit of the *fifth* decimal; that is, the unit-ratio itself is 100,000 inches which is 8,333 feet or 1.58 english mile. Of the three distinct diagrams we shall here insert only the one representing the third ratio, Br/HBr, which is the sharpest and therefore the most decisive. The reduction to centimeter scale by photography is here inserted; for this cut the unit ratio is therefore one kilometer, and the unit of the fifth decimal one centimeter. The gramme is represented by nearly four millimeters. See Plate XXXIV.

Each full black circle represents the determination identified by the same numeral used by Mr. Weber.

The single determinations for less than 60 (no. 7) and for more than 80 grammes (no. 5) of bromine give the mean d of comparatively little importance.

The eight determinations made with between 60 and 80 grammes of bromine fall in two well-defined groups of four determinations each and give the equally important two mean values marked A (1, 3; 2, 10) and B (4, 8; 6, 9) of which C is the final mean.[6]

But it is clear that this mean C cannot be considered to be the true mean value of the ratio r because it is nothing more than the mean of eighth determinations which Mr. Weber made with the eighth weights of bromine which he "happened to take." For as a matter of fact, the eight determinations do not give some constant value from which the individual determinations differ by small deviations equally distributed as to amount and sign. On the contrary, the eight determinations form a well-defined straight line A–B, inclined to the axis. Accordingly, it is *this straight line* A–B itself which represents the eight determinations made by Mr. Weber. Only in case the line A–B were parallel to the axis of weights taken (horizontal in the drawing) and if, at the same time, all deviations were small, could the point C be taken as a legitimate mean.

It is readily seen that the line AB is the geometrical representation of the equation

$$r = 57.7 - 0.113w, \tag{1}$$

where r is expressed in units of the fifth place of decimals and w in grammes of bromine taken. That is: r is *not* a constant, but varies according to the form $k - cw$, where k and c are constants,

We may express the strange fact revealed in the above by saying that the result of the experiment depends on the choice of the weights taken by the chemist, so much so that "we can tell as soon as the weight has been taken and before the experiment has been

---

[6] It may be noted that of the two isolated determinations 7 and 5, the first (7) is made with the smallest weight of bromine and therefore shows the greatest deviation, while the last (5) made with the greatest weight of bromine falls distinctly close to the line AB.

made, what the outcome thereof will be," or perhaps more strikingly still, we might say that "we get (within sufficiently large limits to count) whatever value *r* we would like to get."

But the value of *r* directly determines the value of the atomic weight itself, as we shall show in detail; hence the fact just stated for the ratio applies with equal force to the atomic weight itself.

IV. Systematic Errors and Chemical Perturbations.

The existence of such systematic errors in the most refined laboratory work of renowned chemists, from Stas to the present, is not a new discovery, for I have proved the existence thereof twenty years ago. See the note presented by Berthelot at the Séance of the twelfth of December, 1892.[7]

I here insert (Plate XXXVI.) a reduction to half the original scale of the diagram (no. 215) published in the note just mentioned, together with the diagram (no. 216) of the next note (February 27, 1893). The new cut (no. 752) is a like reduction of Plate I. of my "True Atomic Weights" of 1894 and represents the systematic errors of Stas in his famous syntheses of silver nitrate (no. 251) and of lead nitrate (no. 252). See plate XXXV.

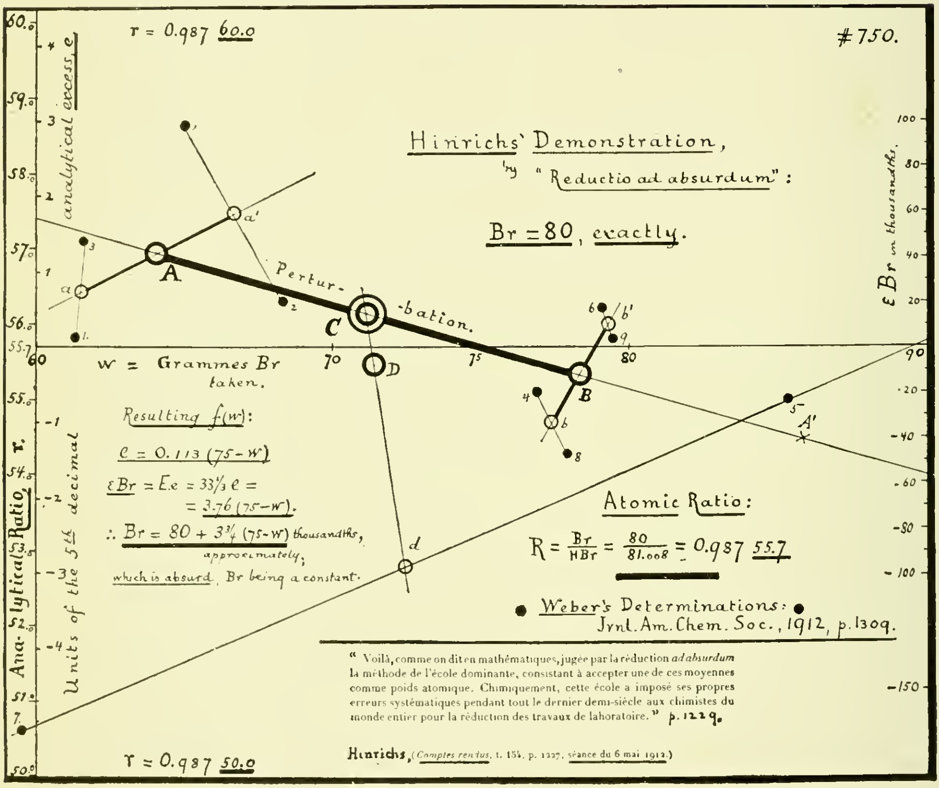
Indeed it is even forty years since I first pointed out the existence of definite *perturbations* (or disturbances) in the chemical work of Stas, namely at the Salem meeting of the American Association for the Advancement of Science in 1869,[8] of which the part here in question is reprinted in my "True Atomic Weights," 1894, pp. 65–69, under the regretfully appropriate heading: vox clamantis in deserto.

We shall, however, in the future restrict the term "chemical perturbation" to such systematic errors as are expressible by a definite function and therefore representable by a definite curve. Such are the systematic errors in the recent work of Mr. Weber, being represented analytically by an equation of the first degree (1) and geometrically by the straight line *A–B* (cut no. 750, Plate XXXIV.).

---

[7] *Comptes Rendus,* T. 115, p. 1074.

[8] *Proceedings,* pp. 112–124.



Hinrichs' Demonstration, by "Reductio ad absurdum":

Br = 80, exactly.

Resulting f(W):

$e = 0.113\,(75-W)$

$\varepsilon Br = E.e = 33\tfrac{1}{3}\,e =$
$= 3.76\,(75-W).$

$\therefore\ Br = 80 + 3\tfrac{3}{4}\,(75-W)$ thousandths, approximately;

which is absurd, Br being a constant.

Atomic Ratio:

$$R = \frac{Br}{HBr} = \frac{80}{81.008} = 0.987\ 55.7$$

● Weber's Determinations: ●
Jrnl. Am. Chem. Soc., 1912, p. 1309.

" Voilà, comme on dit en mathématiques, jugée par la réduction *ad absurdum* la méthode de l'école dominante, consistant à accepter une de ces moyennes comme poids atomique. Chimiquement, cette école a imposé ses propres erreurs systématiques pendant tout le dernier demi-siècle aux chimistes du monde entier pour la réduction des travaux de laboratoire." p. 1229.

Hinrichs, (Comptes rendus, t. 154, p. 1227, séance du 6 mai 1912.)

PLATE I.

Reduced to ½ from:

The True Atomic Weights of the Chemical Elements.

St. Louis and New York, 1894

Fig. 1.

251.

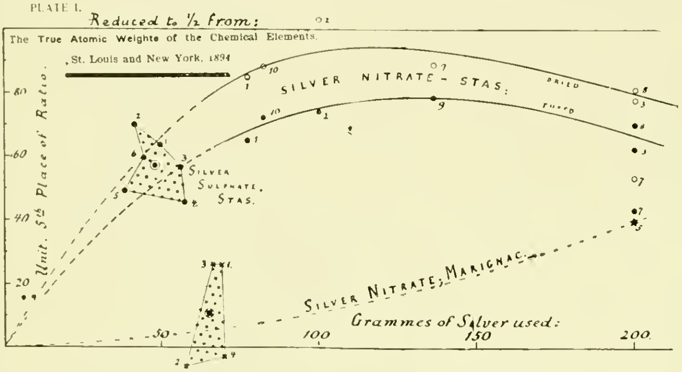
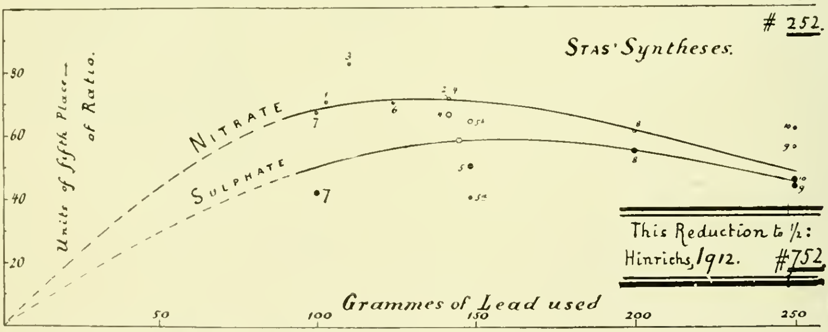
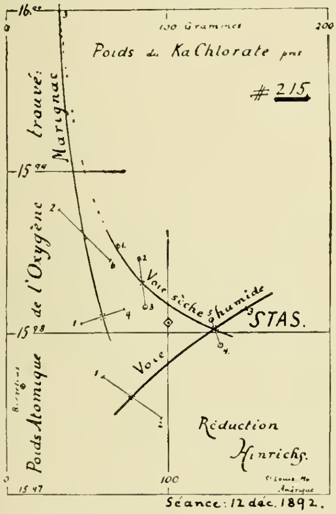


Fig. 2.

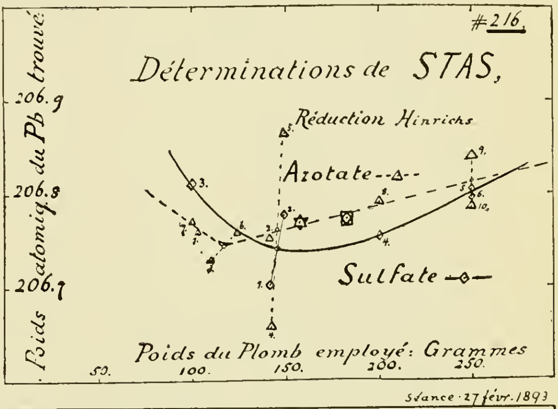
252.



This Reduction to ½:
Hinrichs, 1912. #752.



Séance: 12 déc. 1892.



Séance · 27 févr. 1893

Systematic Errors in the Laboratory Work of Stas, Hinrichs 1892 and 3.
Comptes Rendus, T. 115, p. 1077; T. 116, p. 432. #751.

In fact I have communicated to prominent chemists in the United States and in France first proofs of some of my new cuts representing quite a number of such chemical perturbations. All the dominant elements[9] and a number of the others have now been so represented. These first proofs form already quite an atlas. One of these cuts (no. 737) has been published in the *Comptes Rendus* of the meeting of May 6, 1912.[10] It covers work of Richards at Harvard and of Guye at Geneva, on the dominant elements Ag, Cl and N, O, respectively.

By this work we have also introduced into chemistry the method of demonstration of the geometricians of ancient Greece known as the "*reductio ad absurdum*," which is just as decisive in modern chemistry of precision as in geometry, the highest science of ancient Greece.

V. The Rational Method of Reduction.

This was first published in the *Comptes Rendus* of March 27, 1893 and in my "True Atomic Weights" of 1894. It has been extended and perfected during twenty years, but no complete exposition of all the steps involved having been published in one place at one time, it is no doubt somewhat difficult to grasp and use the same. It is for this reason that we here give, *merely as an example,* its application to the laboratory work of Mr. Weber on bromine.

The old way of successive substitution, producing of necessity an accumulation of errors unknown in magnitude, is based upon the elementary method of solving an algebraic equation with supposedly one unknown only, when in fact it contains as many unknown as there are elements present in the chemical reaction employed. Since, however, in a chemical reaction it is impossible to accept any one element as without error in its action, all these equations are de facto indeterminate (or diophantic) and therefore insoluble. The solutions given by the school are therefore erroneous and cannot be in accord with the facts.

But while the work of the school during the entire century has thus necessarily failed to give a true solution of the problem by that

---

[9] *Comptes Rendus,* T. 153, p. 817; 30 Oct., 1911.

[10] T. 154, p. 1228.

method, it has established incidentally one general fact of great practical importance, namely that all the atomic weights are approximations to certain whole or half numbers, if the atomic weight of oxygen is taken at 16 exactly.

Consequently we may say that the entire mathematical problem will require only the exact determination of the value of this small *departure* (which we now represent by the Greek letter epsilon ϵ).

Every mathematician knows that all relations, even the most complex, are thereby reduced to simple proportions. Hence all our calculations can be carried out by proportional parts, if the necessary relations have first been deduced either by geometry or by development into series. We have used both methods. After overcoming these difficulties we have systematized the work by simple analytical processes, retaining however the general geometrical method for the presentation of the data of experiment and the results of calculation, as exemplified above and in our numerous diagrams of which reductions by photography are printed.

It seems best, at this point, to state the degree of precision aimed at: the third decimal (thousandths) of the atomic weight and the fifth decimal (hundred thousandths) of the ratios (atomic R and analytic r). If at any time we feel authorized to go beyond this general limit, the higher decimals are given as decimals to the above, in order to conform to definitions given and to avoid confusion.

VI. The Departure, ϵ.

The true atomic weight of bromine is known to be some value quite near the number 80; all chemists admit this as an established fact. *Hence we limit our work to the determination of the precise small number of thousandths of the unit, our departure* ϵ.

Accordingly we say: the exact atomic weight of bromine is $80 + \epsilon$. We then perform all analytical operations with this sum instead of using the one symbol Br. Thus many terms will cancel and others will drop out as minute quantities of too high an order to be of influence on the result: facts and processes familiar to all those versed in mathematical work. In this way we finally obtain readily workable formulæ. (See p. 61 of our "Cinquantenaire," 1910, for an example and note the interesting story of its wanderings in 1907 and 1908.) This may be sufficient for the present to direct those readers who may need such reference.

We now return to the simple practical details necessary for carrying out the work of determining the small departure ϵ for bromine.

VII. The Atomic Ratio *R*, and its Variation Δ

To express the chemical reaction used, we first take the departure as zero (that is Br = 80 exactly and H = 1.008 to the nearest thousandth), as we have shown it to be in our history of all determinations for hydrogen made in the century past.[11] This gives us *R* and Δ as shown in Table III. by elementary mathematics.

TABLE III.

Ratio for	1st H/Br	2nd H/HBr	3rd Br/HBr
First, for	Br = 80	and	H = 1.008
Atomic ratio	$\frac{1.008}{80}$	$\frac{1.008}{81.008}$	$\frac{80}{81.008}$
which is $R =$	0.012 60.1	0.012 44.4	0.987 55.7
Second, for	Br = 80.1	and	H = 1.008
Atomic ratio	$\frac{1.008}{80.1}$	$\frac{1.008}{81.108}$	$\frac{80.1}{81.108}$
which is $R' =$	0.012 58.5	0.012 42.9	0.987 57.2
hence $\Delta\mathrm{Br} = R' - R =$	-1.6	-1.5	$+1.5$
Third, for	Br = 80	and	H = 1.108
Atomic ratio	$\frac{1.108}{80}$	$\frac{1.108}{81.108}$	$\frac{80.0}{81.108}$
which is $R'' =$	0.013 85.1	0.013 66.2	0.986 33.9
hence $\Delta\mathrm{H} = R'' - R$ is	125.0	121.8	-121.8

---

[11] *Revue gén. de Chimie,* 1910, 377–389.